National Defense Center for Energy and Environment

Demonstration/Validation of Incremental Sampling at Two Diverse Military Ranges and Development of an Incremental Sampling Tool

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Office of the Assistant Secretary of the Army (Installations and Environment)

The NDCEE is operated by: CTC Concurrent Technologies Corporation

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **JUN 2010**	2. REPORT TYPE	3. DATES COVERED **00-00-2010 to 00-00-2010**

4. TITLE AND SUBTITLE **Demonstration/Validation of Incremental Sampling at Two Diverse Military Ranges and Development of an Incremental Sampling Tool**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **National Defense Center for Energy and Environment (NDCEE),Concurrent Technologies Corporation,100 CTC Drive,Johnstown,PA,15904**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 14-17 June 2010 in Denver, CO. U.S. Government or Federal Rights License

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**46**	

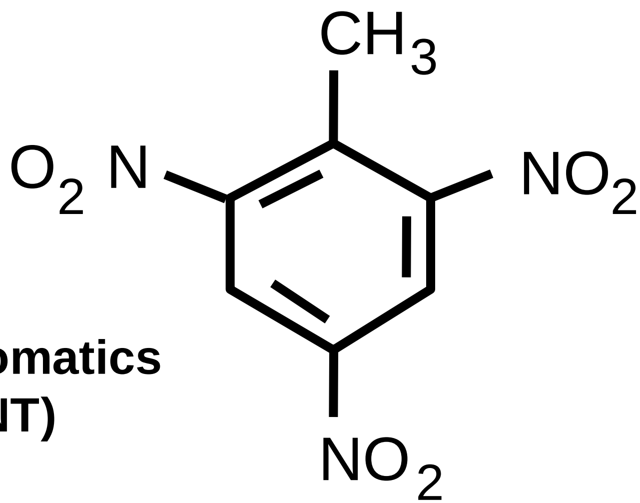
Objectives/Goals

- Reduce uncertainty in site chemical characterization of military ranges by:
  - Demonstrating a reliable soil sampling strategy to accurately characterize contaminant concentrations in spatially extreme and heterogeneous conditions
  - Decreasing potential for missed hot spot characterization
  - Decreasing sampling costs compared to discrete sampling
- Additionally, assessment of:
  - “Scoop off the top” subsampling error
  - Variance among laboratory triplicates
  - Two different grinding techniques in the laboratory
  - Analytical results for different detectors after separation

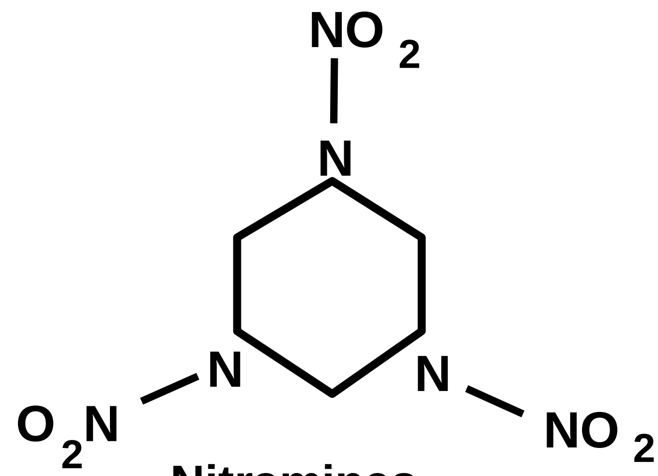
Why is Sampling Conducted at DoD Ranges?

- Major potential problem of migration of energetic compounds off range in aqueous solution
  - Contamination of underground drinking water aquifers (MMR - range closed by EPA)
  - Contamination of surface water bodies
- Ecological risk assessments
  - Eagle River Flats impact range (Ft. Richardson) closed due to water fowl poisoning with white phosphorus
- DoD Directive 4715.11 establishes requirement for each DoD component to assess environmental impacts of munitions use on operational ranges
- MMRP program – For pre-9/30/2002 non-operational, non-permitted sites under DERP

Major Classes of Energetic Compounds Used by DoD

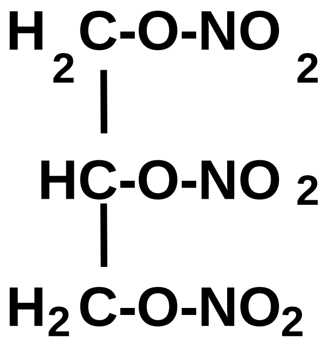


Nitroaromatics (TNT)



Nitramines (RDX)

Nitrate Esters (NG)



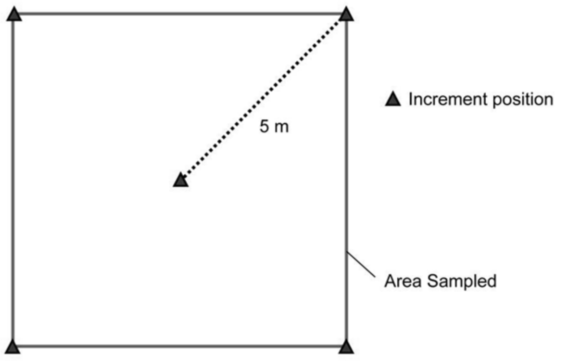
DoD Sites Potentially Contaminated with Energetic Compounds

- Ammunition plants
  - Synthesis
  - Load, assemble, and pack
  - Destruction of off-spec material
- Depots
  - Storage
  - Destruction of out-of-date munitions
- Training and test ranges
  - Impact areas
  - Firing points
  - Demolition ranges

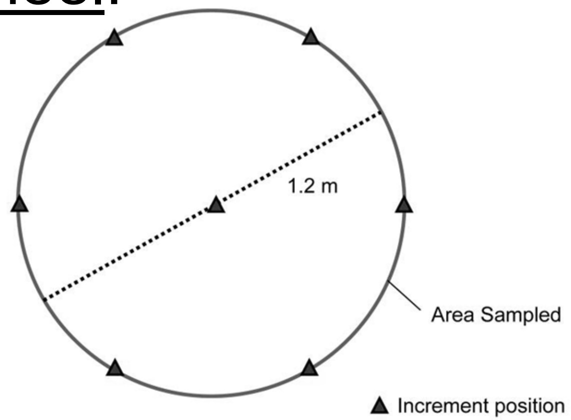
Traditional Sampling Approaches

- Site divided into a set of decision (exposure) units
- One or several discrete or small-scale composite soil samples collected to represent each decision unit
- Analytical results assumed to be normally distributed (and representative)
- Mean (or 95% upper confidence limit) and estimates of uncertainty computed using normal statistics

Box:

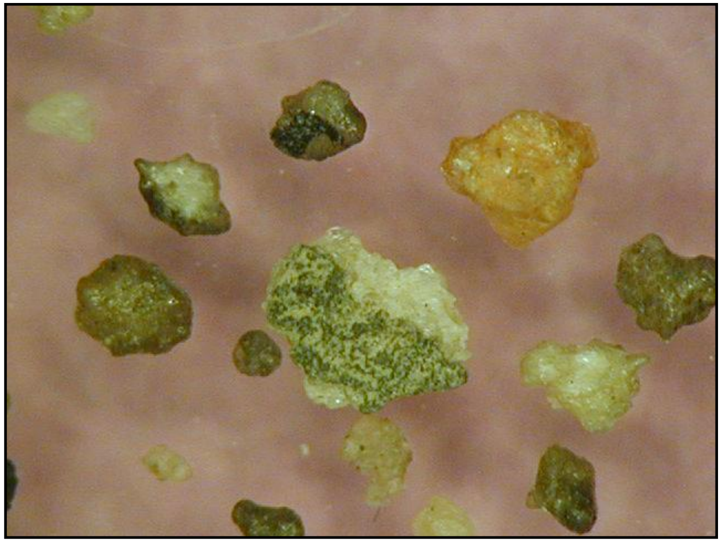


Wheel:



Energetics Residue Deposition

Firing points - particles and fibers of propellant with nitroglycerin (NG) and dinitrotoluene (DNT) w/in nitrocellulose matrix →



← Impact areas - particles of explosives deposited from low-order (partial) detonations

Residues of Composition B Deposited at Impact Areas

- Particles (chunks) of Composition B deposited range in size from micrometer to centimeter
- Soil sized particles are defined as < 2 mm
- One 1-mm spherical particle of Composition B:
  - weighs about 0.9 mg
  - contains ~ 0.50 mg of RDX
    0.35 mg of TNT
    0.05 mg of HMX
- If the soil concentration is 1 mg/kg of RDX, a kilogram sample contains only two of these 1-mm particles
- Energetics deposition results in surficial contamination w/ both distributional and compositional heterogeneity

Representativeness:
Often the Missing Element in QA

- Does the sample collected and shipped to the laboratory adequately represent the exposure area?
- Does the portion of the sample that is used for extraction/digestion adequately represent the sample arriving at the laboratory?
- CRREL research on energetic compounds in soil at training ranges addressed these questions. Method 8330B including *MULTI INCREMENT*® sampling (MIS) field sampling protocol is the result of this research.
- This project provided an independent demonstration/validation of MIS compared to traditional field sampling protocols for energetics

What is *MULTI INCREMENT®* Sampling (MIS)?

- Technique of combining many increments of soil from a number of points within exposure area
- Developed by Enviro Stat (Trademarked term "*MULTI INCREMENT®*"); Researched by CRREL for surface soil sampling at ranges for energetic compounds
- Differs from typical composite in two ways:
  - Number of increments (grabs) much greater (30 minimum)
  - Entire area of interest (decision unit, exposure area) is represented by each sample
- MIS theory is to mitigate single sample variability that results from:
  - discrete (single point) sampling
  - composite sampling with limited increments and/or small areal extent of coverage

More on *MULTI INCREMENT*® Soil Sampling

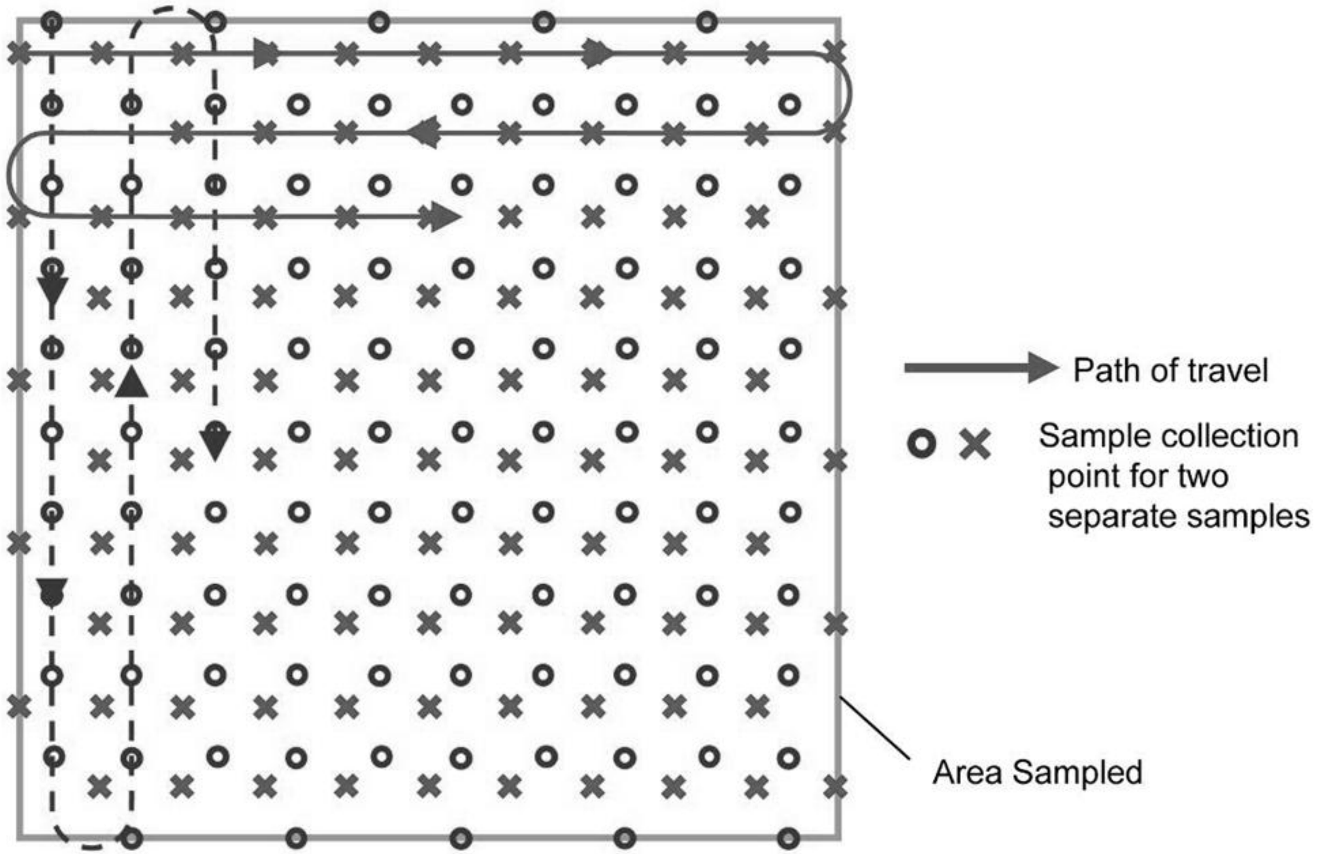
- Balance between number of increments collected, volume of each increment, and depth of sample should result in about 1 to 2 kg of total sample size sent to lab

- Helps address both compositional and distributional heterogeneity

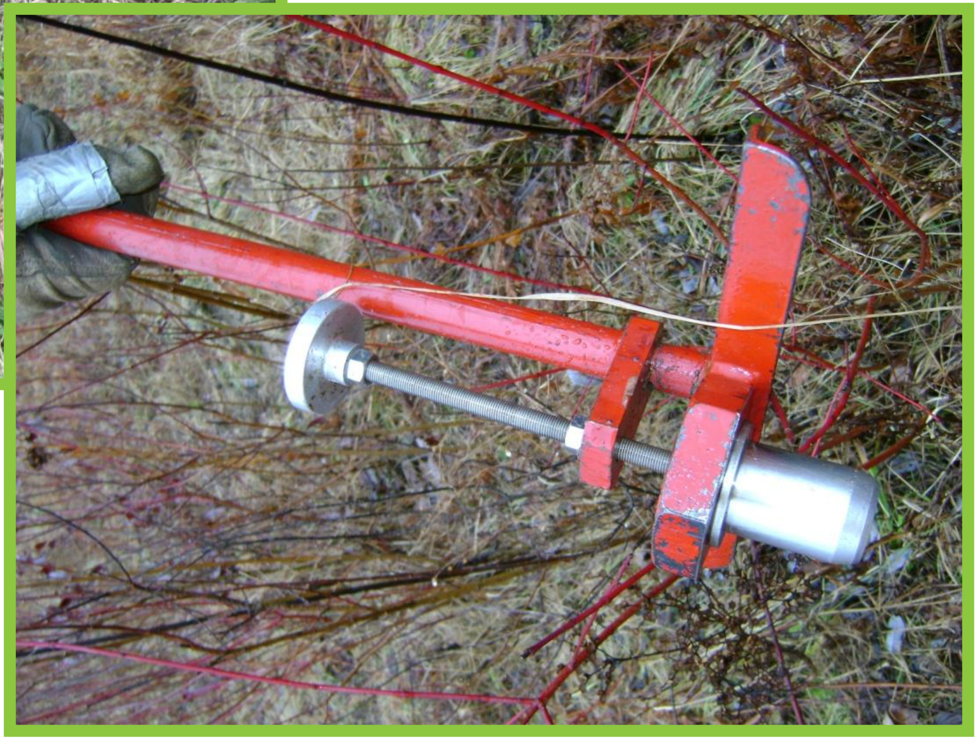
- Normalizes distribution

- This project demonstrated MIS validity compared to the discrete, box, and wheel techniques for a single decision unit at two diverse military ranges by assessing reproducibility (variance) of replicates

Pattern of *MULTI INCREMENT*® sample collection using systematic-random sampling design



Tools for *MULTI INCREMENT*® Sampling



Laboratory Analyses of Energetics by EPA Method 8330A

- Traditional analytical method for surface soil samples resulting from discrete, box, and wheel methods
- Per typical lab protocol, subsampling under 8330A consists of taking a "scoop off the top" of the soil (in-transit settling of sample can lead to unrepresentative lab subsample even from field composite)
- Per 8330A, this subsample is ground with mortar and pestle, and screened w/ 30 mesh sieve, and HPLC/UV extraction and analysis
- Modifications to 8330A for this project
  - 10 mesh (2 mm) sieve size
  - Include nitrogylcerin as a target analyte

Laboratory Analyses of Energetics by EPA Method 8330B

- EPA Method 8330B released in 2006 calls for drying and sieving (10 mesh or 2 mm) entire sample – a subsequent presentation will detail laboratory aspects
- Entire portion <2 mm subjected to grinding, then subsampling is conducted using a MIS technique in the laboratory
- 8330B allows either HPLC/UV or HPLC/MS
- Additional evaluations per 8330B for this project
  - Two different grinding techniques will be used for MI samples (roller ball mill and ring and puck mill)
  - Both UV and MS will be used as detectors for a subset of extracts and results compared

Project Completion

- Government approved Field Sampling and Laboratory Sampling and Analysis Plans
- Draft Final Report submitted to Government
- Field sampling at Red Rio Bombing Range, Live Drop Area, Holloman AFB completed March 2009
  - Impact area - arid bombing range, dry sandy soils, particles
- Field sampling at Range 59, Fort Lewis completed July 2009
  - Firing points - humid firing range, well-drained soils, propellant site
- TestAmerica Laboratories, Inc., Denver, CO analyzed samples
  - All lab managers and bench chemists trained on project requirements
  - 4 discrete; 4 box; 4 wheel; 4 MIS for roller ball mill; 4 MIS for ring and puck mill for analysis
  - QA samples include two soil blanks and two aqueous equipment blanks

Sampling at Holloman AFB

Entering Bombing Range

Sampling at Holloman AFB

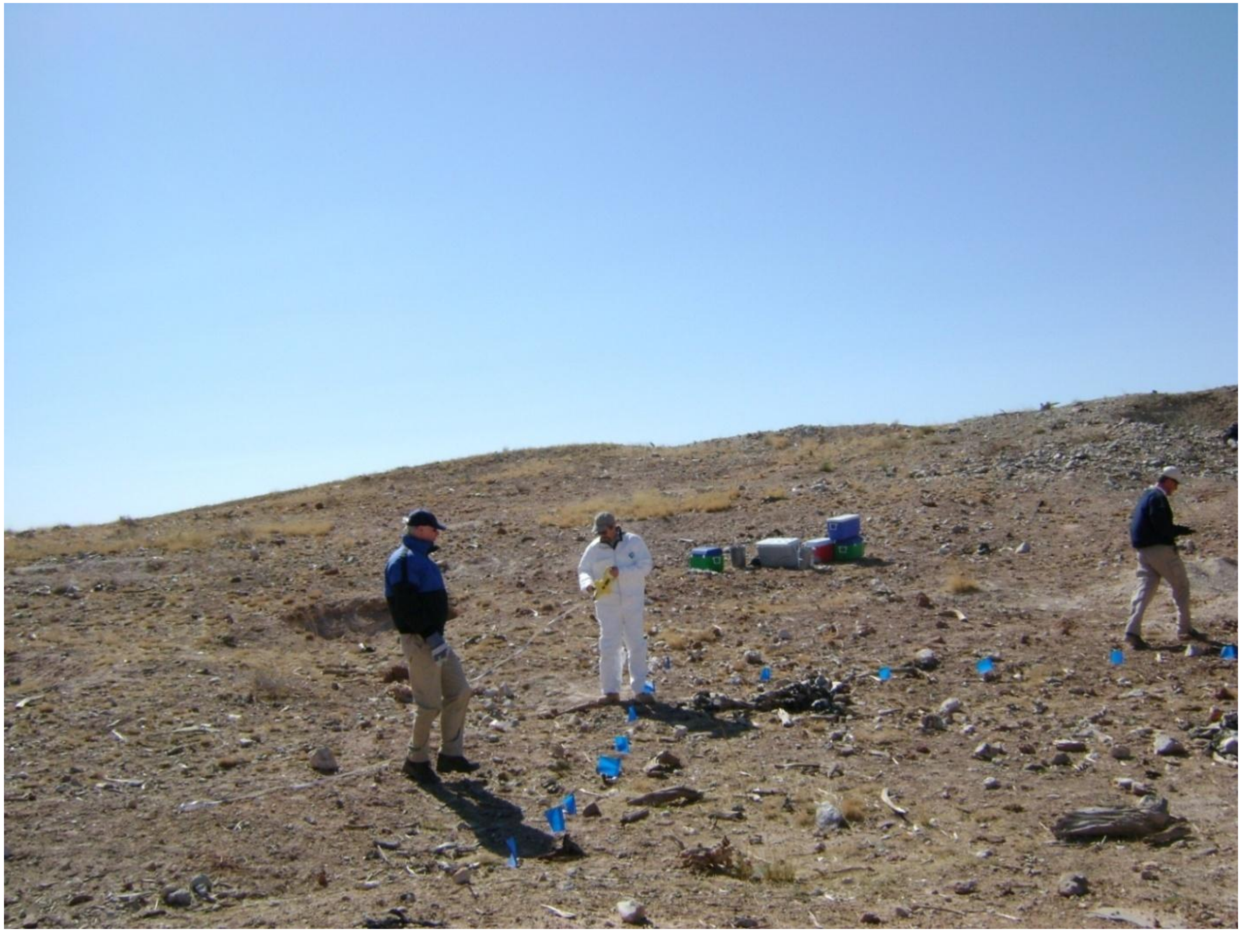
Dropped Bomb Weathering

CRREL Tool Prepared for Sampling

Sampling at Holloman AFB

Meeting with EOD Technician to Finalize Safety Protocol

Sampling at Holloman AFB



Layout of 10 x 10 m Decision Unit (Area of Interest)

Sampling at Holloman AFB

Conducting *MULTI INCREMENT*® Sampling (100 increments/hour)

Sampling at Holloman AFB

Template Set for a Wheel Sample

Sampling at Holloman AFB

Composting the Seven Wheel Increments

Sampling at Holloman AFB

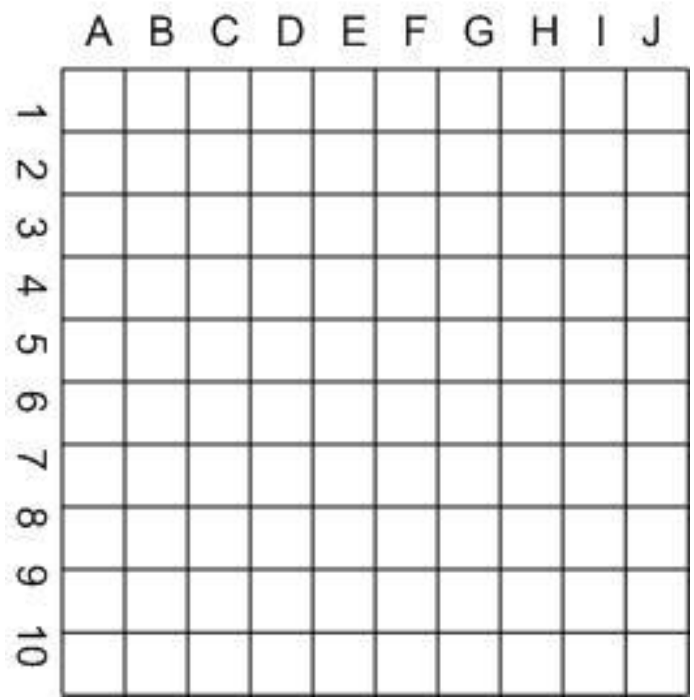
Completing Sample Documentation/QA Sampling/Packing

Sampling at Holloman AFB

Tritonal (TNT with aluminum) from low-order detonation of 2,000-lb bomb

Expray field kit used to verify TNT content

Holloman Decision Unit



- Est. 10 m x 10 m decision unit adj. to crater of low order detonation of 500 lb. bomb
- Tritonal (TNT w/ Al) prime CoC; extremely heterogeneous site
- Collected four reps ea. of discrete, box, wheel, MIS ball mill, and MIS puck mill samples
- All samples 0 – 2.5 cm depth, dry, loose fine to coarse sand w/ very little vegetation
- 100 increments for MI samples

Data Evaluation

- True mean is unknowable; Assess representativeness by “reproducibility”, indicated by variance of data in like groups
- Calculate Mean and Standard Deviation of each like data group
- Calculate % Relative Standard Deviation (% RSD) of each like data group; Compare % RSDs (e.g. data resulting from “scoop off the top” vs. “in-lab MIS procedure”) % RSD = (s*100)/m
- The lower the % RSD for a like data group, the better quality the data in terms of reproducibility, therefore representativeness
- Calculate Relative Percent Difference (RPD) to compare two values (e.g. subsample to bulk sample) RPD = ABS(A-B)/m*100

Holloman Laboratory Replicates
TNT Results (mg/kg)

Sample Type	Replicates			Corrected Bulk	Mean	Range	Std Dev	% RSD	RPD	Range RPD	
	1	2	3							High	Low
Discrete	1900	230	210	1960	780	210-1900	970	124	86	3	161
Box	1100	1800	1500	3260	1470	1100-1800	351	24	76	58	99
Wheel	0.6	0.37	0.47	0.80	0.48	0.37-0.6	0.12	24	50	29	74
MIS-Ball-HPLC/UV	1700	1700	1600	1600	1670	1600-1700	58	3	4	6	0.2
MIS-Ball-HPLC/MS/MS	1600	1300	1400	1590	1430	1300-1600	153	11	11	0	20
MIS-Puck-HPLC/UV	1500	1400	1700	1890	1530	1400-1700	153	10	21	10	30
MIS-Puck-HPLC/MS/MS	1600	1400	1800	1500	1600	1400-1800	200	13	6	18	7

Holloman Field Replicates TNT Results (mg/kg)

Sample Type	Replicates				Mean	Range	Std Dev	% RSD	95% UCL
	1	2	3	4					
Discrete	1900	11	37	200	537	11-1900	913	170	1610
Box	1100	160	6400	3700	2840	160-6400	2800	99	6140
Wheel	0.6	21000	42	90	5280	0.60-21000	10500	198	17600
MIS-Ball-HPLC/UV	1700	1300	2000	3300	2080	1300-3300	866	42	3090
MIS-Ball-HPLC/MS/MS	1600	1100	1500	2900	1780	1100-2900	780	44	2690
MIS-Puck-HPLC/UV	1500	2100	1000	1700	1580	1000-2100	457	29	2110
MIS-Puck-HPLC/MS/MS	1600	2300	1100	1500	1630	1100-2300	499	31	2210

Project Conclusions – Holloman AFB

- Heterogeneous distribution of TNT in arid, sandy soils; 100-increment MIS compared to discrete, box, wheel
- Compared to traditional sampling methods, MIS provided:
  - Better reproducibility of laboratory replicates
  - A more representative subsample than scoop off the top
  - Better reproducibility of field replicates
- On ring and puck mill vs. roller ball mill grinding and detection by UV vs. MS/MS:
  - Differences between grinding methods were not observed at this site; project-specific determinations necessary
  - UV provided slightly better reproducibility than MS/MS; MS/MS may be preferred for some projects for reasons such as detection limits/better resolution

Sampling at Fort Lewis

Entering Range Area

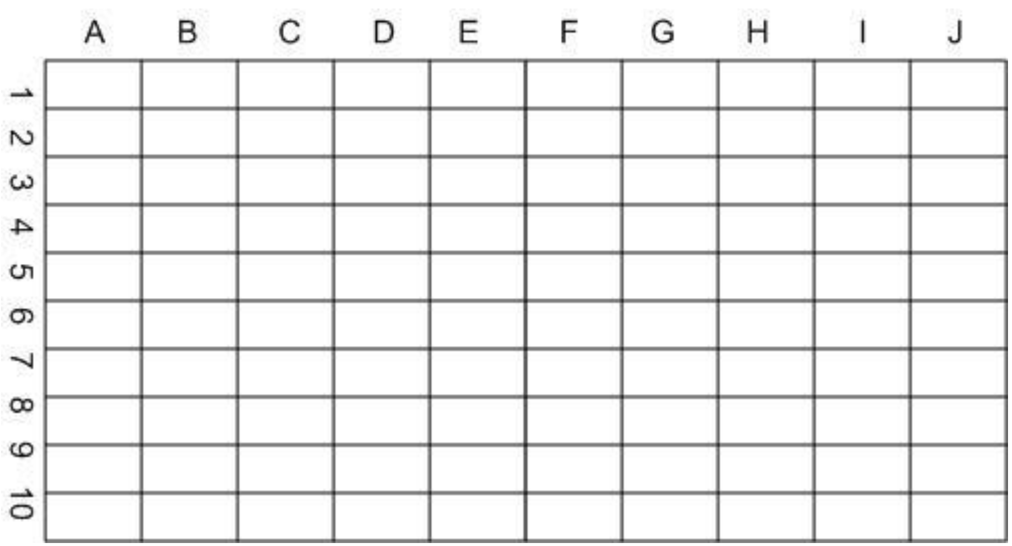
Sampling at Fort Lewis

Decision Unit

Sampling at Fort Lewis

Core from CRREL MIS Tool

Fort Lewis Decision Unit



- Est. 10 m x 20 m decision behind live-fire firing point of M72 LAW and AT-4 Shoulder-fired Rockets
- Nitrogylcerin prime CoC; relatively homogeneous within decision unit
- Collected four reps ea. of discrete, box, wheel, MIS ball mill, and MIS puck mill samples

- All samples 0 – 2.5 cm depth, well-drained, loose sandy loam with some small pebbles
- 100 increments for MI samples

Fort Lewis Live-Fire Laboratory Replicates NG Results (mg/kg)

Sample Type	Replicates			Corrected Bulk	Mean	Std Dev	% RSD	RPD	Range RPD	
	1	2	3						High	Low
Discrete	2390	2020	2110	1590	2170	193	9	31	40	24
Box	5320	4730	4950	2770	5000	298	6	58	63	52
Wheel	2470	2380	2550	2690	2470	85	3	9	5	12
MIS-Ball1-HPLC/UV	1940	---	1880	1820	1910	30	2	5	6	3
MIS-Ball1-HPLC/MS/MS	1870	---	1900	2030	1890	15	1	7	6	8
MIS-Ball6-HPLC/UV	1750	1800	1790	1730	1780	26	1	3	4	1
MIS-Ball6-HPLC/MS/MS	2090	2080	1800	1800	1990	165	8	10	15	0.1
MIS-Puck-HPLC/UV	1630	1630	1650	1580	1640	12	1	3	4	3
MIS-Puck-HPLC/MS/MS	1550	1630	1790	1600	1660	122	7	3	11	3

Fort Lewis Live-Fire Field Replicates NG Results (mg/kg)

Sample Type	Replicates					Mean	Range	Std Dev	% RSD	95% UCL
	1	2	3	4	5					
Discrete	2390	1900	1550	6360	---	3050	1550-6360	2230	73	5680
Box	5320	1520	4200	5120	---	4040	1520-5320	1750	43	6100
Wheel	2470	3490	1800	2400	---	2540	1800-3490	701	28	3370
MIS-Ball-HPLC/UV	1940	1690	1660	1800	1750	1770	1660-1940	110	6	1880
MIS-Ball-HPLC/MS/MS	1870	1760	1440	1700	2090	1770	1440-2090	238	13	2020
MIS-Puck-HPLC/UV	1630	1890	1990	1950	---	1870	1630-1990	162	9	2060
MIS-Puck-HPLC/MS/MS	1550	1970	2140	2120	---	1950	1550-2140	274	14	2400

Project Conclusions – Fort Lewis

- Less heterogeneous distribution of NG in humid, well-drained loam; 100-increment MIS compared to discrete, box, wheel
- Compared to traditional sampling methods, MIS provided:
  - Better reproducibility of laboratory replicates
  - A more representative subsample than scoop off the top
  - Better reproducibility of field replicates
- On ring and puck mill vs. roller ball mill grinding and detection by UV vs. MS/MS:
  - Differences between grinding methods were not observed at this site; project-specific determinations necessary. At high concentration site, homogeneity may be result of mixing rather than mechanical breakdown of nitrocellulose fibers (Jenkins)
  - UV provided slightly better reproducibility than MS/MS; MS/MS may be preferred for some projects for reasons such as detection limits/better resolution

Cost Benefit Analysis Assumptions

- DQO Goal of mean soil concentration in a decision unit
- Equivalent Data Assumptions (to one MIS sample)
  - 30 discrete samples
  - 15 box samples and 15 wheel samples
- One-time Event (Operation & Maintenance not applicable; Travel differences negligible; Mobilization to site not included)
- Surface soils (2.5 cm depth)
- Field QC (two field duplicates (discrete); one field duplicate (box, wheel, MIS)
- Lab QC (MS/MSD for all; LCS for MIS)
- Analytical by HPLC/UV ($150/sample for all, plus $100 prep for each MIS sample)

Cost Benefit Analysis

Expense	30 Discrete	15 Box or Wheel	One 30-increment MIS
Labor ($75/hr)	8 hrs $600	12 hrs $900	4 hrs $300
Method-Specific Equipment*	$125	$150	$1300
Misc. Equipment	$100	$100	$100
Shipping	$400	$175	$100
Laboratory Analysis	$5,250	$2,850	$1,350
Cost to characterize one decision unit	$6,475	$4,175	$3,150
Cost to characterize ten decision units	$62,725	$39,500	$18,900

*Assumes purchase of an IS pogo-stick style sampler

Validation of EVC Soil Stick

- EVC Soil Stick used in Fort Lewis to collect eight replicate samples (0-2.5 cm depth) of 100 increments each
- Same decision unit as discrete, box, and wheel data
- Four samples analyzed by EPA 8330B using puck mill grinding; HPLC/UV

Fort Lewis Live-Fire Laboratory Replicates NG Results Using EVC Tool (mg/kg)

Sample Type	Replicates			Mean	Std Dev	% RSD
	1	2	3			
Discrete	2390	2020	2110	2170	193	9
Box	5320	4730	4950	5000	298	6
Wheel	2470	2380	2550	2470	85	3
MIS-Puck-HPLC/UV	2230	2250	2220	2233	2	0.1

Fort Lewis Live-Fire Field Replicates NG Results Using ECV Tool (mg/kg)

Sample Type	Replicates				Mean	Range	Std Dev	% RSD	95% UCL
	1	2	3	4					
Discrete	2390	1900	1550	6360	3050	1550-6360	2230	73	5680
Box	5320	1520	4200	5120	4040	1520-5320	1750	43	6100
Wheel	2470	3490	1800	2400	2540	1800-3490	701	28	3370
MIS-Puck-HPLC/UV	2230	2020	1830	1680	1940	1680-2230	238	12	2220

Technical Comparison of Soil Sampling Methods

- Hot Spots - a 30- to 100-increment MIS sample will more likely incorporate hot spots to be included in results
- Applicability
  - Wide variety of ranges and settings studied for characterization of energetics
  - Expansion to additional parameters under study
  - Laboratory procedure modification needed
  - Comparisons to historical data
- Laboratory availability – full sample processing for MIS
- Alternate applications and sampling depth – cost-effectiveness likely more dependent on analytical savings

Multi Increment Sampling Status

- Regulatory status and conditions of acceptance
  - Many states have accepted use of MIS; Some require it
- Mr. Alan Hewitt, formerly of U.S. ACE, ERDC-CRREL, Completed Cost and Benefit report focusing on MIS for ranges in ESTCP-funded project
- U.S. ACE, ERDC-CRREL, SERDP-funded project to evaluate expansion of MIS to metals contamination at ranges just beginning
- Interstate Technology and Regulatory Council (ITRC) work group on Multi Increment Sampling evaluating MIS for expanded use

Multi Increment Sampling Benefits

- Time for MIS increment collection in field same or less than traditional methods
- Fewer MI samples needed for equivalent data variability compared to discrete or box or wheel
- Accepted as most representative sampling technique for surface soil sampling for energetics residues at military ranges
- Studies underway to expand MIS for use with additional contaminants and depths/applications (SERDP– metals at ranges; ITRC MIS Team – theory; DOE – mixed contaminants pre- and post-removal of soils)

National Defense Center for Energy and Environment

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This work was funded through the Office of the Assistant Secretary of the Army (Installations and Environment) and conducted under contract W74V8H-04-D-0005 Task 527 A3. The views, opinions, and/or findings contained in this paper are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision unless so designated by other official documentation.